

## Main-Group Compounds

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## Crystalline Divinyldiarsene Radical Cations and Dications

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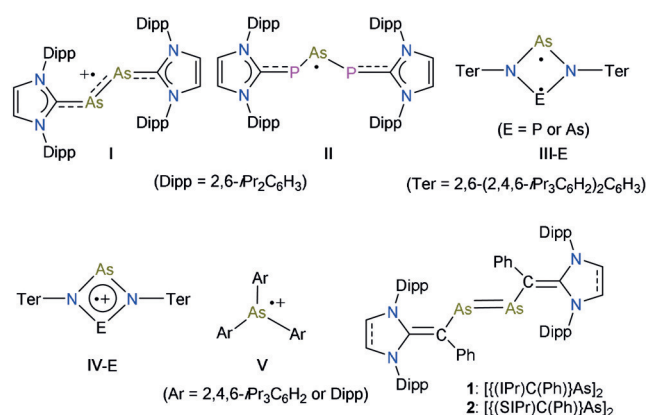
Dedicated to Professor Lothar Weber on the occasion of his 75th birthday

**Abstract:** The divinyldiarsene radical cations  $[(\text{NHC})\text{C}(\text{Ph})\text{As}]_2(\text{GaCl}_4)$  ( $\text{NHC} = \text{IPr}$ :  $\text{C}\{(\text{NDipp})\text{CH}\}_2$  **3**;  $\text{SIPr}$ :  $\text{C}\{(\text{NDipp})\text{CH}_2\}_2$  **4**;  $\text{Dipp} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ) and dications  $[(\text{NHC})\text{C}(\text{Ph})\text{As}]_2(\text{GaCl}_4)_2$  ( $\text{NHC} = \text{IPr}$  **5**;  $\text{SIPr}$  **6**) are readily accessible as crystalline solids on sequential one-electron oxidation of the corresponding divinyldiarsenes  $[(\text{NHC})\text{C}(\text{Ph})\text{As}]_2$  ( $\text{NHC} = \text{IPr}$  **1**;  $\text{SIPr}$  **2**) with  $\text{GaCl}_3$ . Compounds **3–6** have been characterized by X-ray diffraction, cyclic voltammetry, EPR/NMR spectroscopy, and UV/vis absorption spectroscopy as well as DFT calculations. The sequential removal of one electron from the HOMO, that is mainly the As–As  $\pi$ -bond, of **1** and **2** leads to successive elongation of the As=As bond and contraction of the C–As bonds from **1/2**  $\rightarrow$  **3/4**  $\rightarrow$  **5/6**. The UV/vis spectrum of **3** and **4** each exhibits a strong absorption in the visible region associated with SOMO-related transitions. The EPR spectrum of **3** and **4** each shows a broadened septet owing to coupling of the unpaired electron with two  $^{75}\text{As}$  ( $I = 3/2$ ) nuclei.

Stable radicals are appealing synthetic targets in main-group chemistry<sup>[1]</sup> because they challenge conventional bonding paradigms as well as exhibit intriguing electronic structure and physical properties. Among the heavier Group 15 elements (P, As, Sb, Bi), numerous phosphorus-centered stable radicals<sup>[2]</sup> have been isolated and structurally characterized.

However, the number of crystallographically characterized arsenic,<sup>[2g,k,p,3]</sup> antimony,<sup>[4]</sup> and bismuth<sup>[5]</sup> radicals remained limited.

In 2013, Robinson et al. reported the first stable arsenic radical cation **I** (Figure 1)<sup>[3a]</sup> by one-electron oxidation of an N-heterocyclic carbene (NHC)-stabilized diatomic arsenic compound  $(\text{IPr})_2\text{As}_2$ .<sup>[6]</sup> Grützmacher and co-workers



**Figure 1.** Structurally characterized arsenic-centered radicals I–V and divinyldiarsenes **1** and **2**.

reported the neutral radical **II** containing NHC-phosphinidene substituents.<sup>[2k]</sup> Schulz et al. isolated singlet diradicaloids **III-E** ( $\text{E} = \text{P}$  or  $\text{As}$ ) featuring a  $6\pi$ -electron four-membered  $\text{N}_2\text{E}_2$  ring with a considerable open-shell character.<sup>[2g,3b]</sup> Consequently, **III-E** undergo one-electron oxidation to afford the  $5\pi$ -electron radical cations **IV-E**.<sup>[2p]</sup> Very recently, Wang and co-workers reported the radical cations  $\text{Ar}_3\text{As}^+$  (**V**) ( $\text{Ar} = i\text{Pr}_3\text{C}_6\text{H}_2$  or  $i\text{Pr}_2\text{C}_6\text{H}_3$ ).<sup>[7]</sup> The high-lying HOMO of **III-E** and  $\text{Ar}_3\text{As}$  facilitates one-electron oxidation giving rise to radical cations **IV-E** and **V**, respectively. We recently reported crystalline divinyldiarsenes **1** and **2** derived from classical NHCs, which exhibit remarkably small HOMO–LUMO energy gap of 3.86 eV and 4.24 eV, respectively.<sup>[8]</sup> The high-lying HOMO of **1** (–4.42 eV) and **2** (–5.28 eV) encouraged us to probe the synthetic viability of corresponding stable radical cations on one-electron oxidation of **1** and **2**. Herein, we report the synthesis of crystalline divinyldiarsene radical cations  $[(\text{NHC})\text{C}(\text{Ph})\text{As}]_2(\text{GaCl}_4)$  ( $\text{NHC} = \text{IPr}$ :  $\text{C}\{(\text{NDipp})\text{CH}\}_2$  **3**;  $\text{SIPr}$ :  $\text{C}\{(\text{NDipp})\text{CH}_2\}_2$  **4**;  $\text{Dipp} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ) as well as dications  $[(\text{NHC})\text{C}(\text{Ph})\text{As}]_2(\text{GaCl}_4)_2$  ( $\text{NHC} = \text{IPr}$  **5**;  $\text{SIPr}$  **6**).

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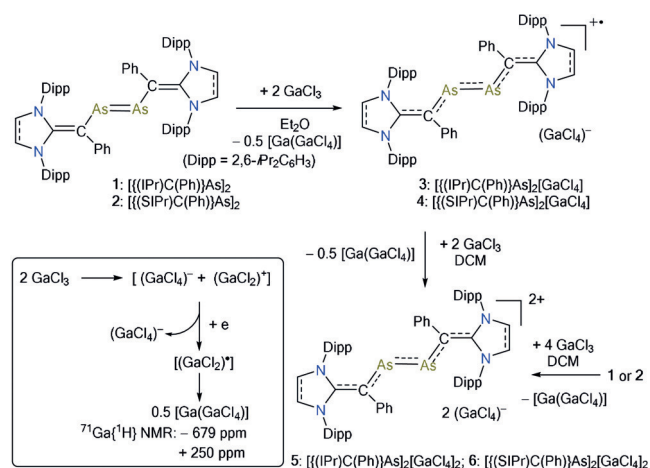
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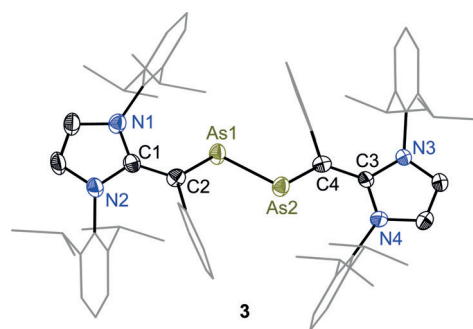
We commenced our studies with electrochemical analyses of **1** and **2** (see the Supporting Information). The cyclic voltammograms (CVs) of **1** and **2** exhibit two one-electron redox events (**1**:  $-1.00$ ,  $-0.67$ ; **2**:  $-0.92$ ,  $-0.51$  V), which may be tentatively assigned to the related radical cations (**1** or **2**)<sup>•+</sup> and dications (**1** or **2**)<sup>2+</sup>, respectively (Supporting Information, Figure F1 and Table T5). One additional wave at  $-1.28$  V was observed for **1** and is most likely associated with the reduction to the corresponding radical anion. However, this wave is absent in the CV of **2**. Accordingly, treatment of an Et<sub>2</sub>O solution of **1** (green) and **2** (violet) each with two equivalents of GaCl<sub>3</sub> immediately led to the precipitation of a dark green solid. After workup, the radical cations **3** and **4** were isolated as green crystalline solids (Scheme 1). The use of an excess GaCl<sub>3</sub> should be avoided as it leads to the over oxidized products, the dications **5** and **6**. Indeed, reactions of **3** and **4** with two equivalents of GaCl<sub>3</sub> quantitatively gave **5** and **6**, respectively. Alternatively, **5** and **6** are also accessible in one-pot reaction of **1** or **2** with four equivalents of GaCl<sub>3</sub>.



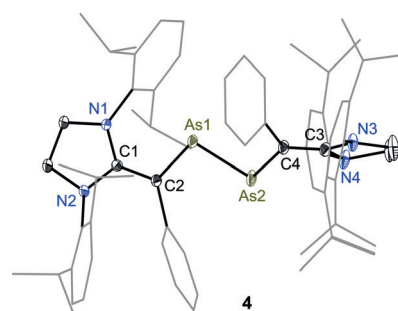
**Scheme 1.** Synthesis of divinyldiarsene radical cations **3** and **4** as well as dications **5** and **6**. Reduction of GaCl<sub>3</sub> into [Ga(GaCl<sub>4</sub>)] (inset) via disproportionation of the putative GaCl<sub>2</sub> intermediate.

Two molecules of GaCl<sub>3</sub> are required for one-electron oxidation of **1** and **2**. The putative oxidizing species is (GaCl<sub>2</sub>)<sup>+</sup> that is formed according to  $2 \text{ GaCl}_3 \rightleftharpoons (\text{GaCl}_4)^- + (\text{GaCl}_2)^+$ . The reduction of (GaCl<sub>2</sub>)<sup>+</sup> yields GaCl<sub>2</sub>, which eventually disproportionates to form the stable mixed-valence Ga<sup>I</sup>/Ga<sup>III</sup> compound [Ga(GaCl<sub>4</sub>)] (Supporting Information).<sup>[9]</sup> Compounds **3–6** are stable under an inert gas atmosphere but readily decompose when exposed to air. Compound **3** and **4** were NMR-silent, thus indicating their paramagnetic nature. The dications **5** and **6** are red crystalline solids and exhibit well-resolved <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR signals for the N-heterocyclic vinyl (NHV) moieties (Supporting Information).

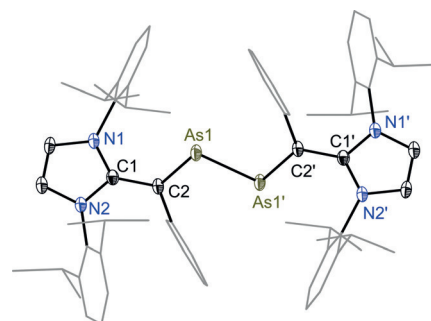
Solid-state molecular structures of **3** (Figure 2), **4** (Figure 3), **5** (Figure 4), and **6** (Supporting Information, Figure F8) were determined by X-ray diffraction, which exhibit the intact As–As bond with *trans*-bent geometries along the two-coordinated arsenic atoms. The HOMO of diarsenes **1** and **2** is the  $\pi$ -orbital of the As=As bond.<sup>[8]</sup> Thus,



**Figure 2.** Molecular structure of divinyldiarsene radical cation **3** determined at 100 K. Ellipsoids are set at 50% probability. Hydrogen atoms, solvent molecules, and the counterion (GaCl<sub>4</sub>) are omitted for clarity.<sup>[12]</sup>



**Figure 3.** Molecular structure of divinyldiarsene radical cation **4** determined at 100 K. Ellipsoids are set at 50% probability. Hydrogen atoms, solvent molecules, minor occupied disordered atoms, and the counterion (GaCl<sub>4</sub>) are omitted for clarity.<sup>[12]</sup>



**Figure 4.** Molecular structure of divinyldiarsene dication **5** determined at 100 K. Ellipsoids are set at 50% probability. Hydrogen atoms, solvent molecules, and the counterions (GaCl<sub>4</sub>) are omitted for clarity.<sup>[12]</sup>

the formation of **3** and **4** as well as **5** and **6** is the result of sequential one electron removal from the HOMO of **1** and **2**. Clearly, this leads to a steady increase in the As–As bond length of **3** (2.322(1) Å) and **5** (2.419(1) Å) as well as **4** (2.330(1) Å) and **6** (2.414(1) Å) with respect to those of **1** (2.296(1) Å) and **2** (2.290(1) Å) (Table 1). The C2–As1/C4–As2 bond lengths of **3** (1.867(4) Å) and **4** (av. 1.876(2) Å) are shorter compared to that of **1** (1.919(1) Å) and **2** (1.936(3) Å) respectively. The C1–C2/C3–C4 bond lengths of **3** (1.424(5) Å) and **4** (av. 1.420(2) Å) are however rather stretched with respect to those of **1** (1.376(2) Å) and **2** (1.369(3) Å).

**Table 1:** Selected bond lengths [Å] and angles [°] of diarsenes (**1**, **2**) and the corresponding radical cations (**3**, **4**) and dications (**5**, **6**).

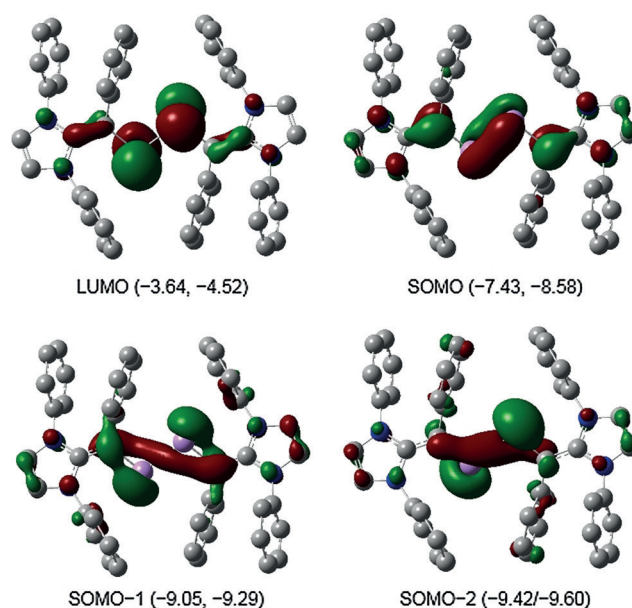
	As–As <sup>[a]</sup>	C2–As1 C4–As2	C1–C2 C3–C4	C1–N1/N2 C3–N3/N4	N1–C1–N2 N3–C3–N4
<b>1</b> <sup>[b]</sup>	2.296(1)	1.919(1)	1.376(2)	1.405(2)/1.395(2)	104.4(2)
<b>3</b>	2.322(1)	1.867(4) 1.867(3)	1.424(5) 1.424(4)	1.368(4)/1.364(5) 1.359(4)/1.368(4)	105.7(3) 105.9(3)
<b>5</b> <sup>[b]</sup>	2.419(1)	1.833(3)	1.451(4)	1.354(4)/1.355(4)	107.2(2)
<b>2</b> <sup>[b]</sup>	2.290(1)	1.936(3)	1.369(3)	1.398(3)/1.397(3)	107.3(2)
<b>4</b>	2.330(1)	1.873(2) 1.880(2)	1.427(2) 1.412(2)	1.356(2)/1.364(2) 1.370(2)/1.369(2)	109.67(1) 108.94(1)
<b>6</b>	2.414(1)	1.839(3) 1.822(3)	1.463(4) 1.469(3)	1.335(3)/1.335(4) 1.334(3)/1.334(3)	111.4(2) 111.5(2)

[a] As1–As1'/As1–As2. [b] Molecular structure features crystallographic center of inversion (C).

This can be rationalized as the increase of the formal positive charge on the arsenic atoms of **3** and **4** leads to the  $\pi$ -electron density transfer from the vinylic C=C bond to the arsenic atom.

As expected, a more pronounced trend in the elongation of As1–As1'/As2 and C1–C2/C3–C4 bonds while the contraction of the C2–As1/C4–As2 bond lengths of dications **5** and **6** is observed compared to radical cations **3** and **4**. The As–As bond length of **5** (2.414(4) Å) and **6** (2.414(4) Å) is longer than that of radical cations **3** (2.322(5) Å) and **4** (2.330(1) Å), however it is still shorter compared to an As–As single bond (ca. 2.46 Å).<sup>[10]</sup> Moreover, the C2–As1/C4–As2 bond lengths of **5** (1.836(3) Å) and **6** (av. 1.830(3) Å) are longer than the C=As double bond length of arsalkenes (1.75–1.79 Å).<sup>[11]</sup> The As–As–C angle in **1** (99.0(1)°) and **2** (98.7(1)°) is comparable with that of the corresponding radical cations **3** (av. 99.7(1)°) and **4** (98.0(5)°). The same in dications **5** (95.7(9)°) and **6** (av. 96.3(8)°) is however marginally smaller. These features suggest the presence of a conjugated C<sub>2</sub>As<sub>2</sub>C<sub>2</sub>  $\pi$ -electron system.

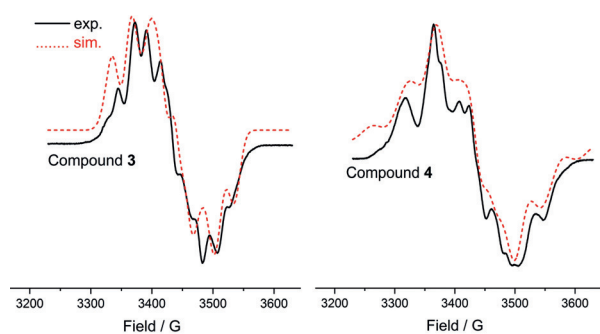
Further insights into the electronic structures of **3–6** were obtained by DFT calculations. The optimized geometries of **3–6** at the M06-2X/def2-TZVPP//M06-2X/def2-SVP level of theory (Supporting Information) show good agreement with their solid-state structures. The computed NPA atomic partial charges (Supporting Information, Table T4) indicate that the As<sub>2</sub> fragment in **3** (+0.40e), **4** (+0.47e), **5** (+0.57e), and **6** (0.62e) carries a positive charge, which is higher than that in **1** (+0.27e) and **2** (+0.32e).<sup>[8]</sup> Each of the vinyl (C2/C4) carbon atoms of **3** (–0.54e), **4** (–0.56e), **5** (–0.47e), and **6** (–0.50e) bears a negative, whereas the carbenic carbon (C1/C3) of **3** (+0.42e), **4** (+0.52e), **5** (+0.41e), and **6** (+0.55e) bears a positive charge. The WBIs (Wiberg bond indices) for the As–As bond of **3** (1.25), **4** (1.24), **5** (1.00), and **6** (0.99) as well as for the C2/C4–As bonds of **3** (1.21), **4** (1.19), **5** (1.54), and **6** (1.53) indicate the delocalization of  $\pi$  electrons over the C<sub>2</sub>As<sub>2</sub>C<sub>2</sub> framework. The SOMO (singly occupied molecular orbital) of **3** (Figure 5) and **4** (Supporting Information, Figure F14) is the  $\pi$ -orbital of the As=As bond, whereas the LUMO (lowest unoccupied molecular orbital) is the  $\pi^*$  orbital of the As=As bond. In contrast, the HOMO of **5** (Supporting Information, Figure F15) and **6** (Supporting Information, Figure F16) is the  $\pi$ -type orbital mainly located



**Figure 5.** Molecular orbitals (isovalue 0.04) of the radical cation **3** calculated at M06-2X/def2-TZVPP//def2-SVP level of theory with energies (eV) for both ( $\alpha$ ,  $\beta$ ) spin states. Hydrogen atoms as well as isopropyl groups are omitted for clarity.

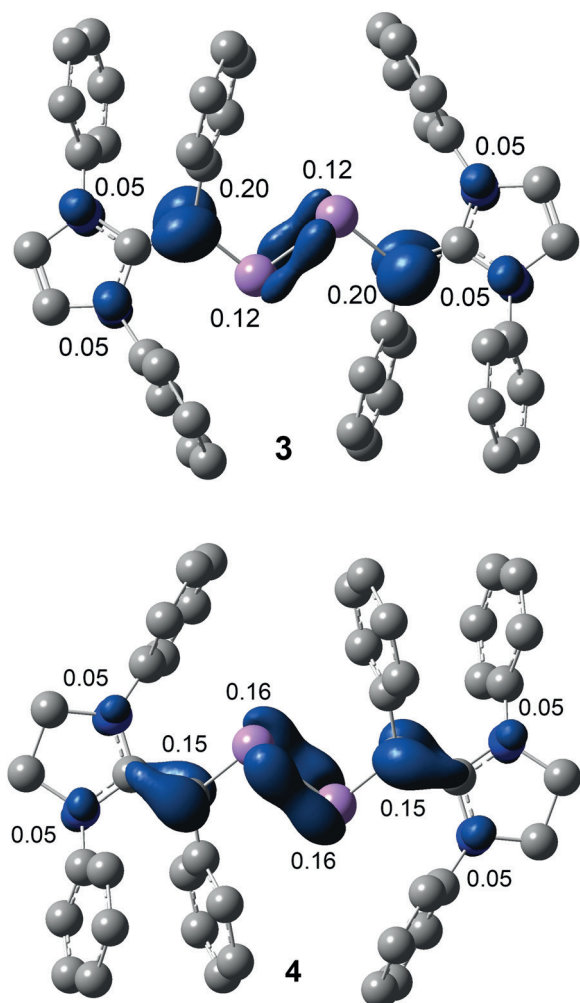
at the C<sub>(Ph)</sub>–As bond. The LUMO of **5** and **6** is the  $\pi^*$  orbital located at the C<sub>2</sub>As<sub>2</sub>C<sub>2</sub> unit. The UV/Vis spectrum of **3** (Supporting Information, Figure F2) and **4** (Supporting Information, Figure F3) each exhibits three main absorption bands, which are red-shifted in comparison to those of **1** and **2**.<sup>[8]</sup> Based on TD-DFT calculations, the band at 822 nm (**3**) and 811 nm (**4**) may be assigned to the SOMO related (S→L and S-1→L) transitions.

The EPR spectra of **3** and **4** were recorded in THF at 9.63 GHz. At 298 K, **3** and **4** exhibit a featureless singlet (Supporting Information, Figures F6 and F7) while at 80 K a broadened septet with poorly resolved hyperfine components was observed because of coupling with two magnetically equivalent <sup>75</sup>As nuclei (Figure 6). These features are similar to those of the radical cation **I** (Figure 1) reported earlier by Robinson and co-workers.<sup>[3a]</sup> The EPR spectra were simulated by using the g values, the hyperfine couplings of each As and *ortho* hydrogen atoms of the phenyl groups, and three linewidth parameters to take into account unresolved hyperfine couplings (Supporting Information, Table T11).



**Figure 6.** X-Band EPR spectra of **3** and **4** at 80 K in THF ( $\nu$  = 9.63 GHz, Mod. Amp. 5G,  $P_{mw}$  = 2 mW).

The calculated Mulliken atomic spin density for **3** and **4** (Figure 7) reveals that the unpaired electron is mainly located at the  $\pi$ -conjugated  $\text{CAs}_2\text{C}$  framework (Supporting Information, Table T10). In **3**, 12% of spin-density is located at each



**Figure 7.** Mulliken spin densities calculated at M06-2X/def2-TZVPP//def2-SVP (isovalue 0.04) of **3** and **4**.

of the arsenic atoms whereas the spin density at each of the vinylic carbon atoms is 20%. The spin density at each of the ring nitrogen atoms of **3** and **4** is 5%. Remarkably, the spin density at the original carbene carbon atom is negligible. In comparison with **3**, the spin density at the arsenic atoms (16% each) of **4** is higher compared to that of **3** (12% each). Furthermore, the spin density at the vinylic carbon atoms (15% each) of **4** is lower with respect to that of **3** (20% each). This is most likely due to the puckered (non-planar) structure of 1,3-imidazoline rings of **4** that twist the vinylic  $\text{C}=\text{C}$  bond out of the  $\text{As}=\text{As}$  bond plane, leading to a diminished  $\pi$  conjugation compared to that in **3** featuring planar 1,3-imidazole rings. This is also revealed in the X-ray structures of **3** and **4** (Figures 2 and 3). The  $\text{C}_3\text{N}_2$  ring plane angle of **3** ( $6.53(14)^\circ$ ) is considerable smaller compared with that of **4** ( $83.33(11)^\circ$ ). Similarly, the  $\text{C}2\text{-As}1\text{-As}2\text{-C}4$  torsion angle of  $178.57(14)^\circ$  in **3** is larger than that in **4** ( $163.37(8)^\circ$ ).

In conclusion, the first diarsene radical cations **3** and **4** as well as the dications **5** and **6** have been prepared as crystalline solids. All compounds **3–6** have been characterized by EPR/NMR and UV/vis spectroscopy, and X-ray diffraction and analyzed by computational studies. In accessing **3–6** from **1** and **2**,  $\text{GaCl}_3$  functions as an oxidizing agent and two equivalents of  $\text{GaCl}_3$  are required for one-electron oxidation. The formation of mixed-valence  $\text{Ga}^{\text{I}}/\text{Ga}^{\text{III}}$  compound [ $\text{Ga}(\text{GaCl}_4)$ ] as the main-side product has been shown with  $^{71}\text{Ga}\{\text{H}\}$  NMR spectroscopy. Experimental and theoretical results suggest that the radical cations **3** and **4** are stabilized by the delocalization of unpaired electron over the  $\text{CAs}_2\text{C}$ -unit. DFT calculations reveal that the spin density is mainly located at the arsenic (12% in **3** and 16% in **4** on each As) and vinylic carbon (20% in **3** and 15% in **4** on each C) atoms.

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### Conflict of interest

The authors declare no conflict of interest.

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